

High rate reactive ion etching of Al_2O_3 and Si

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The reactive ion etch rate (RIE) of Al_2O_3 -based ceramics, in a plasmax reactor with a gas mixture of 5 μm Ar and 2 μm Cl_2 , is temperature sensitive. The etch rate at room temperature (~ 2600 Å/min) is essentially all physical sputtering. For $T = 250^\circ\text{C}$, the etch rate increase to ~ 8200 Å/min. This increase in etch rate is the "chemical" component of the total etch rate. By means of the same technique, etch rates up to 2.0 $\mu\text{m}/\text{min}$ were obtained for Si. In contrast to physical sputtering, RIE of these materials has the advantage that the reaction products are volatile compounds. Redeposition problems should therefore be minimized. In addition, the increase in etch rate obtained by RIE can be used as a trade-off to optimize other process parameters.

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I. INTRODUCTION

We have recently been interested in developing an acceptable process to etch deep (~ 12 μm) patterns in Al_2O_3 based ceramics. At the moment, the process that is used to etch patterns into these ceramics is physical sputtering at a rate ~ 250 Å/min, requiring etch times of several hours. However, it is well-known that during the process a great deal of previously etched material is redeposited on top of the etched sidewall. This redeposited material, which is a problem for certain applications, is of course inherent to the sputter etch process. It would be desirable therefore to identify an alternative process in which redeposition is minimized, and at the same time one in which the etch rate is increased. The reactive ion etching (RIE) process is an attractive candidate. A key feature of the RIE process is that active species from the electric discharge combine chemically with the target material to form a chemical compound that is volatile. The etched products in the gaseous state are then pumped out of the system rather than being redeposited as they are in normal physical sputtering. It is also likely that a higher etch rate will be achieved with RIE than with physical sputtering since both chemical plasma etching and physical sputtering occur simultaneously. From the standpoint of an initial investigation it seems desirable to seek the highest RIE rate possible to reduce the etch time and to minimize debris build up.

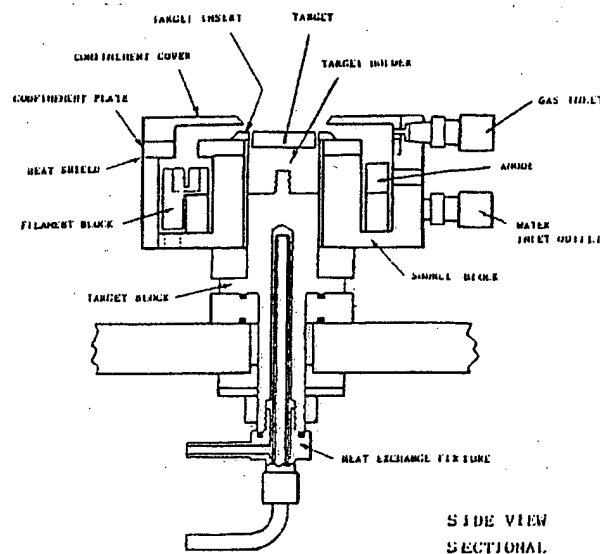
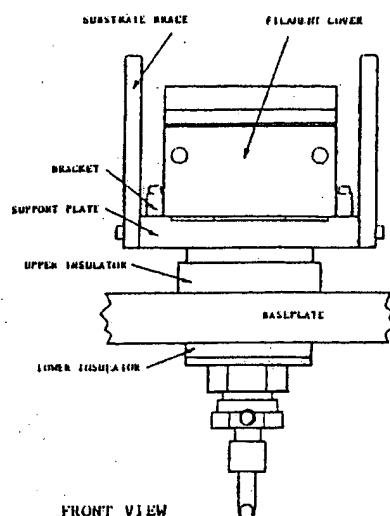
II. RESULTS AND DISCUSSION— Al_2O_3

As a first step one needs to determine what etch products would be volatile. The ceramic material is primarily Al_2O_3 . An examination of tables of physical properties for Al based chemical compounds shows that of all the simple compounds (preferably Al with one other element), AlCl_3 has the lowest boiling point (182°C) and the highest vapor pressure at room temperature. An examination of the tables for the other constituent of the ceramic shows that its chloride also has a low boiling point and high vapor pressure. The RIE process is therefore most easily done with a Cl based gas. A number of choices are possible, but three of the simplest gases are Cl_2 , CCl_4 , and BCl_3 .

A number of RIE geometries are also possible. We have access to a low pressure diode system and a hot filament triode system.^{1,2} In plasma etching, the etching gas is converted into chemically active species by electron impact dissociation processes. By consideration of glow discharge mechanisms, it can be shown that the current density at the target electrode can be taken as a measure of the generation rate of active species. In a typical diode system the degree of ionization is of the order of 10^{-4} , with a resulting target current density of about 1 mA/cm². The hot filament triode system makes more efficient use of electron impact dissociation. The degree of ionization is typically 10^{-2} , sometimes as high as 10^{-1} , with a resulting target current density on the order of 100 mA/cm². In our work we investigated RIE in both the diode and hot filament triode configuration.

The initial experiment was done in the diode configuration to determine whether in fact "chemical" etching did occur at an accelerated rate. A substrate of the ceramic was attached to a quartz target, and then covered by a half-mask of glass. The etch rate of the sample was then determined for two conditions; one in which the etchant gas was CCl_4 , and the other in which the gas was Ar. In both conditions the pressure of the gases was 6 μm , and the target electrode voltage was ~ 600 V. No attempt was made to control or measure the sample temperature. Because it was mounted on an insulating SiO_2 target immersed in a plasma, we suspect the sample was above room temperature. A pure argon plasma was first used to estimate, in a crude way, the extent of physical sputtering. In both cases the sample was placed outside the target dark space. Thus virtually no physical sputtering or ion-assisted plasma etching can occur, but chemical etching should, due to the reactive species produced in the discharge. The etch rates were 440 Å/min in CCl_4 and 7 Å/min in Ar. The observed sputter etch rate in Ar was, as expected, nearly zero and the chemical etch rate was thus over 400 Å/min. If the sample was inside the dark space, and we assume a typical additional physical sputter etch rate of ~ 250 Å/min in both gases, the total rate would be ~ 690 Å/min in CCl_4 . The initial result was encouraging. It showed that "chemical" etching was in fact occurring.

FIG. 1. The figure contains cross-section views of the model 210 Plasmax (L. M. Simard Co.).



The hot filament triode system is a commercially available unit called a "Plasmax," supplied by L. M. Simard Co. A schematic diagram of the apparatus is shown in Fig. 1. We have added a metallic screen to cover the target opening.³ The screen improved the stability of operation and further confined the plasma which resulted in a higher current density and higher etch rate.

As mentioned earlier, one expects the hot filament triode etch rate to be significantly higher than obtainable by diode sputtering. We found that the physical sputter etching rate of the ceramic was 2500 Å/min under the following conditions: Ar pressure = 7 μm, the hot filament discharge current $I_p = 4$ A, and target bias voltage $V_t = -500$ Vdc. This physical sputter rate was independent of target temperature.

We next investigated the results of adding a reactive gas. A stable discharge could be sustained in pure BCl₃. However, we found that a carrier gas, such as Ar, was needed to stabilize the discharge for CCl₄ and Cl₂. We settled on a gas mixture of 5 μm of Ar plus 2 μm of Cl₂ as a standard mixture. This choice resulted in good plasma stability, and high etch rate. BCl₃ and CCl₄ also produced good results but produced an unneeded complication, which was contamination of the system with decomposition reaction products (i.e., B and C). To reduce the physical sputter etch rate (i.e., to enhance the ratio of chemical etching to physical etching), we attempted to substitute H₂, He, and O₂ for Ar, but found that these gas mixtures would not produce a suitably stable discharge.

Under the same conditions as described above, but with the Ar-Cl₂ mixture replacing pure Ar, we observed a rate of 3100 Å/min for a room temperature target. Since one can expect that the physical sputter yield of Cl₂ is not very different from that of Ar, this would suggest that the combined physical and chemical etch rate under these conditions is only about 25% greater than the physical sputter etch rate alone.

The rate was found to be very temperature dependent (see Fig. 2). With all conditions the same as above but with the sample temperature raised to 150°C, the etch rate increased to over 7000 Å/min, and with the temperature raised further to 250°C, the etch rate increased to over 8000 Å/min. This observation is evidence that the reaction products are volatile. We do not claim that the rate limiting step (steps) for the reaction rate is the volatility of the reactive products. It is however instructive to calculate the temperature dependence of AlCl₃ in this temperature regime, and this is given by⁴

$$P = \exp \left(37.2 - \frac{13860}{T} \right), \quad (1)$$

where P is in mm of Hg and T is in degrees K. Thus at room temperature (300 K), the vapor pressure of AlCl₃ is approximately 0.0001 mm. At 150°C, AlCl₃ has a vapor pressure of about 85 mm. At both these temperatures, the chloride of the

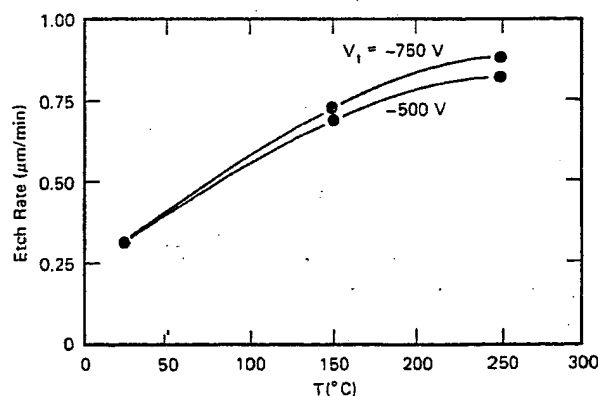


FIG. 2. This shows the temperature dependence of the etch rate of the ceramic sample in composite gas containing 5 μm Ar and 2 μm Cl₂.

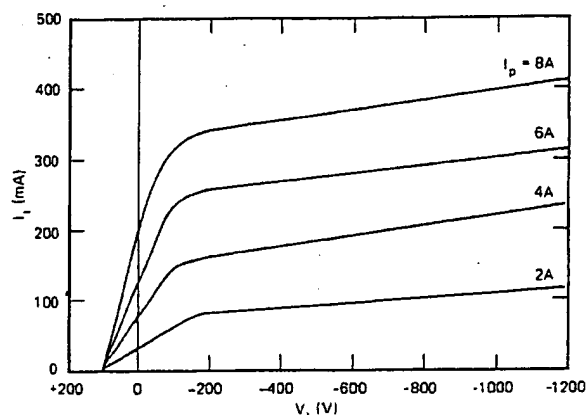


FIG. 3. The figure shows the target current versus target voltage characteristic of the Plasmax reactor.

other component of the ceramic has a higher vapor pressure. 250°C is above the atmospheric boiling point of both compounds. At room temperature, the vapor pressure of AlCl_3 is small, so that the main etch reaction product is not markedly volatile at room temperature. By 150°C all etch products have a large vapor pressure; the etch rate can therefore markedly increase.

We also observed that raising the target bias voltage from -500 Vdc to -750 Vdc did not significantly raise the etch rate. This is understandable if the etching action is primarily chemical. A typical target current/target voltage characteristic for the Plasmax is shown in Fig. 3. It can be seen that the target current is roughly independent of target voltage for values of V_t beyond about -100 Vdc. Thus increasing the target bias beyond -100 Vdc will increase the physical sputtering yield but will have little effect upon the chemical reaction rate. With this in mind, we attempted to increase the ratio of chemical etching to physical sputtering by lowering V_t below -500 Vdc. However, the etch rates for $V_t = -250$ Vdc were erratic and unreproducible, and in many instances a black deposit was observed to form on the target surface. It would appear that a bias voltage of -500 Vdc is required to produce consistent results.

III. PROBLEM AREAS— Al_2O_3

The generation of reactive ion species is proportional to the discharge current. In a pure $7\text{ }\mu\text{m}$ Ar atmosphere, the Plasmax has been operated at $I_p \geq 20$ A, thus a potential fivefold increase in etch rate is possible (i.e., a rate of over $4\text{ }\mu\text{m}/\text{min}$). Although we are able to operate at higher currents in an argon plasma, at the moment we are not able to operate the device in a Cl_2 containing atmosphere with $I_p > 6$ A because the anode melts.¹ It is reasonable to assume that this problem can be eliminated by designing a water-cooled anode structure, as it has in the hot filament system used for the earlier work.²

Another problem is associated with masks. The rather hostile environment of the intense Cl plasma in the Plasmax at temperatures over 100°C resulted in the destruction of photoresist masks and of a stainless steel contact mask. We achieved some success with an evaporated MgO mask. With

a $0.8\text{-}\mu\text{m}$ -thick MgO mask we are able to etch features $1.2\text{ }\mu\text{m}$ deep. The problem with any mask material, including MgO, is that the physical sputtering yield of most materials is higher than that of the ceramic. Thus even though RIE increases the etch rate of the ceramic by about a factor of 4, the total etch rate is still comparable to the physical sputter etch rate of most other materials. As a consequence it would appear that the mask thickness must be on the order of the depth to be etched. This problem should not be considered a real limitation because ultra-thick masks are required for the present physical sputter etch process. In the case of RIE, this problem can perhaps be mitigated somewhat by further experimentation to determine a stable gas mixture which has a higher ratio of chemical to physical etch rate. For example, by operating at a lower target voltage.

The use of Cl presents a number of technical problems for a production situation. The Cl plasma is destructive to most standard vacuum pumps, rubber (viton/neoprene) gaskets, pump oils and lubricants, aluminum and even stainless steel vacuum parts. For routine use with Cl, the apparatus would require special design with corrosion resistant components. Furthermore, AlCl_3 volatilized at the target will condense on other parts of the vacuum chamber. AlCl_3 is deliquescent so that upon opening the vacuum chamber to atmosphere, considerable quantities of water condense onto the chamber fixtures. One possible solution is to bake the entire system to $T \sim 150^{\circ}\text{C}$ before venting the chamber to vaporize all the condensed AlCl_3 , and pump it away. While problems of this sort do exist, they are not insurmountable. In fact, chlorine-based discharges have been used for years, and are currently being used to etch fine structures for microcircuits.⁵

IV. ETCHING OF SILICON

Plasma etching of silicon is now a standard process. The various systems commercially available all produce etch rates $\sim 1000\text{ }\text{\AA}/\text{min}$, which is adequate in microcircuit fabrication where thicknesses to be etched are quite small. However, there are other applications where much greater thicknesses must be etched. Wet chemical processing is normally used in such cases, but plasma etching could offer many advantages, including vertical etch profiles, if higher etch rates could be obtained.

V. RESULTS—Si

Using the same rationale and equipment that was used to etch the ceramic material, we etched Si in a gas mixture of $5\text{ }\mu\text{m}$ Ar and $4\text{ }\mu\text{m}$ CF_4 . With a main discharge current of 5 A, an etch rate of $1.75\text{ }\mu\text{m}/\text{min}$ was achieved for Si. Increasing the current to 6 A produced an etch rate of $2.0\text{ }\mu\text{m}/\text{min}$. The lack of cooling of the anode prohibited larger currents, but with adequate cooling and the maximum useable current of 12 A, etch rates for Si $\sim 4\text{ }\mu\text{m}/\text{min}$ should be obtainable.

VI. CONCLUSION

RIE with a chlorine-based gas is an attractive alternate way of etching Al_2O_3 based ceramics. The two advantages of the process are (1) the reaction products are volatile compounds and (2) the chemical etch rates are high. The first, we expect

will minimize redeposition, and the second can, if necessary, be used as a trade-off to optimize other process parameters. The main problem area is the question of mask material.

Also using the hot filament triode plasma etching technique, silicon has been etched at rates of 2 $\mu\text{m}/\text{min}$, and higher rates should be obtainable.

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